## INTRODUCTION

Fluoride exists fairly abundantly in the earth's crust and enter groundwater through natural process. Low levels of fluoride are required for humans as it has beneficial effects on tooth and bone structures. However, ingestion of excessive fluorides, mainly through drinking water causes dental, skeletal and non skeletal fluorosis. Long term ingestion of excessive fluoride has a chronic effect on the kidneys as well, the optimum level suggested by WHO is 0.7 ppm from infancy to 16 years of age. According to the WHO, the maximum acceptable concentration of fluoride ions in drinking water is 1.5ppm, to prevent dental and skeletal fluorosis (Figure-1).

Dental fluorosis**,** also called mottling of tooth enamel**,** is a developmental disturbance of dental enamel caused by excessive exposure to high concentrations of fluoride during tooth development. The risk of fluoride overexposure occurs at any age but it is higher at younger ages. In its mild forms (which are its most common), fluorosis often appears as unnoticeable, tiny white streaks or specks in the enamel of the tooth. In its most severe form, tooth appearance is marred by discoloration or brown markings. The enamel may be pitted, rough and hard to clean. The spots and stains left by fluorosis are permanent and may darken over time.

Dental Fluorosis

Skeletal Fluorosis

Figure-1

## PART LITERATURE REVIEW

It is considered that probable source of high fluoride in Indian waters is that during raining and circulation of water in rocks and soils, fluorine is leached out and dissolved in groundwater. The fluoride content of groundwater varies greatly depending on the

type of rocks from which they originate. Among the various minerals responsible for high concentration of fluoride, the Fluorapatite $Ca_3(PO_4)_2.CaF_2$ and $CaF_2$ are important. Concerned with the magnitude of health problems due to excess concentration of fluoride in drinking water, several methods of defluorination of drinking water have been developed. The ion-exchange, adsorption, reverse osmosis and precipitation are the usual means of defluorination. However, in India precipitation and adsorption methods are most preferred. The adsorption method involves the contact of the fluoride containing water with a suitable adsorbent. Precipitation process is based on the adition of chemicals and removal of insoluble compounds as precipitates.

In adsorption method, different types of adsorbents are being used for defluorination and removal of other minerals, dyes and heavy metals e.g. activated alumina [1], coconut shell carbon [2], baggase [3], chemically activated carbon[4], bone charcoal [5], natural zeolites[6], burn clay [7], crushed clay pots [8], electrodialysis[9] and other low cost bioadsorbents like saw dust [10], used tea leaves, cow dung[11] have been found to be highly effective, cheap and eco-friendly.

The shortcomings of most of the methods are high operational and maintenance costs, low fluoride removal capacity, lack of selectivity for fluoride, undesirable after effects on water quality, generation of large amount of sludge and complicated procedure. The most commonly available method in India, Nalgonda Technique of community defluoridation, is based on precipitation process and is very efficient and cost effective. The main limitation of this technique are daily addition of chemicals, large amount of sludge production, less effective with water having high total dissolved solids and high hardness. Besides it converts a large portion of ionic fluoride (67-87%) into insoluble aluminium complex and practically removes only a small portion of fluoride in the form of precipitate (18-33%).Therfore, this technique is erroneous[12] . Residual aluminium ranges from 2.01-6.86 ppm was reported in Nalgonda technique, which is dangerous to human health as aluminium is a neurotoxin and its concentration as low as 0.08ppm in drinking water has been reported to cause Alzheimer's disease[13] and has strong carciogenic properties[14].

Adsorption methods are effective on both terms i.e. fluoride removal and cost for removal. Hence the need to find locally available defluorination media for less expensive and technically feasible in rural communities level is desirable.

In the present study, we are proposing a defluorination of drinking water by employing Brick Powder (BP) and Marble Slurry Powder (MSP) as new, feasible, effective and low cost adsorbents. Both BP and MSP are industrial wastes and available in abundance, creating various environmental problems and challenges related to their management. We are trying these adsorbents to defluorinate water in different locations of Jaipur City of Rajasthan State.

By using BP and MSP as adsorbents we are not only trying to solve the Fluoride problem of water but also, addressing the Waste management problems associated thereof. In this regard, the study is absolutely a green approch.

## DESCRIPTION OF THE STUDY AREA

### Geographical Details of Rajasthan [15]

Rajasthan is located in the north western part of the subcontinent. It is bounded on the west and northwest by Pakistan, on the north and northeast by the states of Punjab, Haryana, and Uttar Pradesh, on the east and southeast by the states of Uttar Pradesh and Madhya Pradesh, and on the southwest by the state of Gujarat. The Tropic of Cancer passes through its southern tip in the Banswara district. The state has an area of 132,140 square miles (3,42,239 $km^2$) and subdivided in 33 districts. The capital city is Jaipur.

Figure 2: Map of Rajasthan State.

In the west, Rajasthan is relatively dry and infertile; this area includes some of the Thar Desert, also known as the Great Indian Desert. In the south western part of the state, the land is weter, hilly, and more fertile. The climate varies throughout Rajasthan. On average winter temperatures range from 8° to 28° C (46° to 82° F) and summer temperatures range from 25° to 46° C (77° to 115° F). Average rainfall also varies; the western deserts accumulate about 100 mm (about 4 inches) annually, while the south eastern part of the state receives 650 mm (26 inches) annually, most of which falls from July through September during the monsoon season[16.]

**Geographical Details of Jaipur[17]**

Geographical area of Jaipur district is 11,117.8 $Km^2$. Total number of villages is 2380. It is situated in the east of Rajasthan state. It is bounded by Sikar district on the North, Haryana state on the extreme northeast, Alwar and Dausa districts on the east ,Sawai Madhopur district on the southeast ,Tonk district on the south, Ajmer district on the west, and Nagaur district on the northwest. East and North area of Jaipur district is surrounded by Aravalli hills.

Figure3: Map of Jaipur

The important rainy rivers of Jaipur are Ban Ganga and Sabi. To provide drinking water to old city there is Ramgarh dam on Ban Ganga river. There is a single natural lake named Sambhar lake, the water of which is salty and is the largest source of good

quality salt in India. Height of it is 122 to 183 meters from sea level. Total length of district from East to West is 180 Km. and total width from North to South is 110 Km.

Area: 11117.8 $km^2$

Altitude: 431 meters

Temperature:

| maximum | minimum | |
|---|---|---|
| 45 | 25 | Summer |
| 22 | 05 | Winter |

Languages: English, Hindi, Rajasthani

Population Status (as per 2011 Census)

Total Population: 66,63,971

Urban: 34,99,204

Rural: 31,64,767

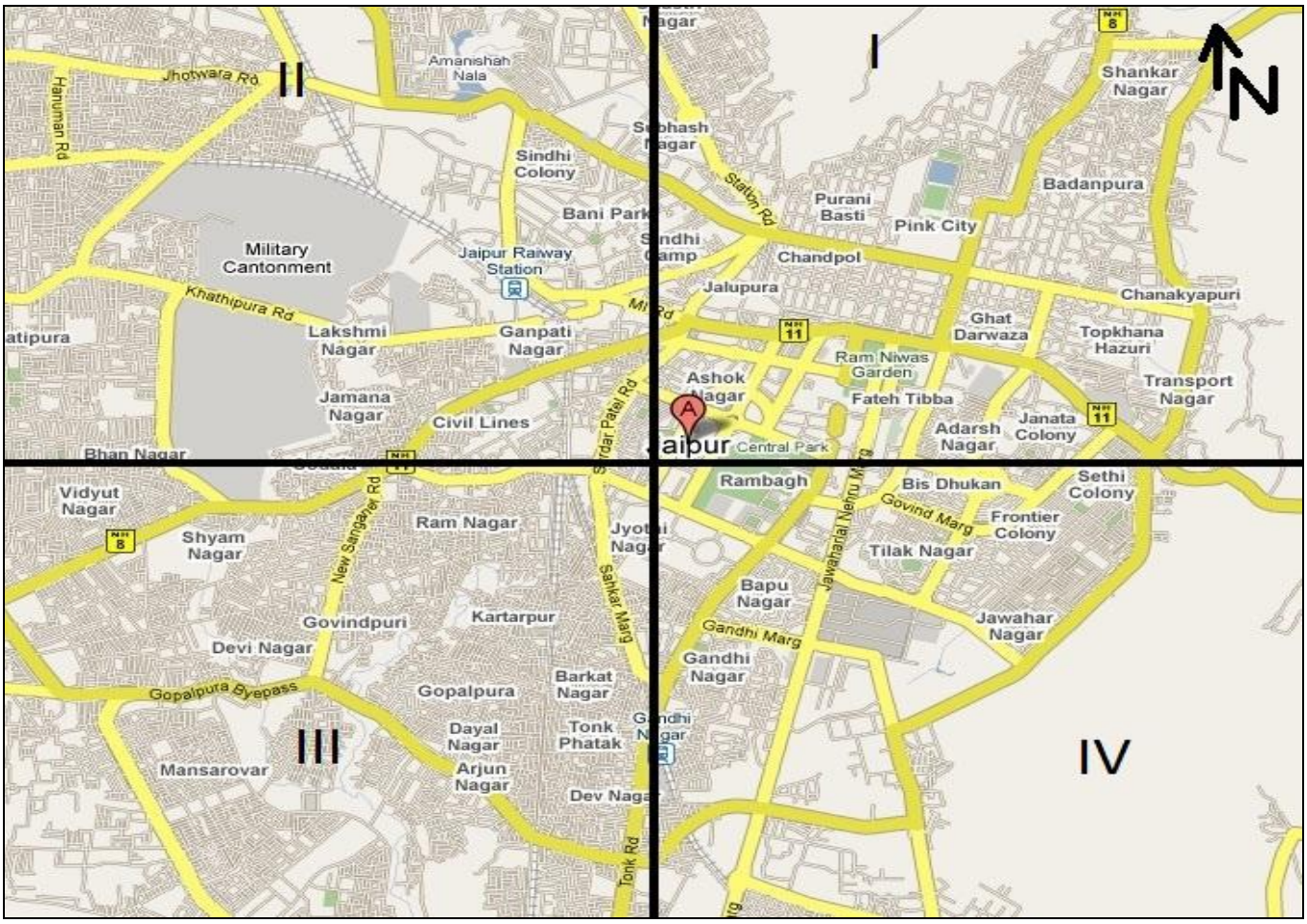
Male: 34,90,787

Female: 31,73,184

Jaipur City has a humid subtropical climate, receiving over 650 millimetres (26 inches) of rainfall annually but most rains occur in the monsoon months between June and September. Temperature remains relatively high throughout the year, with the summer months of April to early July having average daily temperatures of around 30 °C (86 °F). During the monsoon there are frequent, heavy rains and thunderstorms, but flooding is not common. The winter months of November to February are mild and pleasant, with average temperatures ranging from 15–18 °C (59–64 °F) and with little or no humidity. There are however occasional cold waves that lead to temperatures near freezing.

Jaipur is the 10th largest city of India according to census of 2011. 47.49% People live in rural areas, 52.51% live in urban areas.

The Study Area (Jaipur City) is divided into four different zones for convenience of the present study, as follows-




ZONE- I

1. Shankar Nagar
2. Badanpura
3. Chanakyapuri
4. Ghat Darwaza
5. Tophkhana Hazuri
6. Transport Nagar
7. Ramniwas Garden
8. Fateh Tibba
9. Adarsh Nagar
10. Ashok Nagar
11. Jalupura
12. Sindhi camp
13. Janta Colony

ZONE- II

1. Bani Park
2. Sindhi Colony
3. Jhotwara
4. Military Area
5. Civil lines
6. Laxmi Nagar

7. Jamana Nagar
8. Ganpati Nagar
9. Bhan Nagar
10. Khatipura

ZONE- III

1. Shayam Nagar
2. Ram Nagar
3. Vidyut Nagar
4. Govindpuri
5. Devi Nagar
6. Jyoti Nagar
7. Kartarpura
8. Gopalpura
9. Barkat Nagar
10. Tonk phatak
11. Devi Nagar
12. Mansarover

ZONE- IV

1. Rambagh
2. Bapu Nagar
3. Frontier Colony
4. Tilak Nagar
5. Sethi Colony
6. Jawahar Nagar
7. Gandhi Nagar
8. Malviya Nagar
9. Jagatpura
10. Pratap Nagar

**STATEMENT OF THE RESEARCH PROBLEM**

"Removal of Fluoride from water of Jaipur city by using Industrial Wastes: A Green Approach"

**OBJECTIVES OF THE STUDY**

1. To study physicochemical characteristics including fluoride content of water present in different locations of the Jaipur city.
2. To make an attempt for defluorination of drinking water by employing brick powder and marble slurry as new, feasible, effective and low cost adsorbents.
3. To compare water quality of different zones of Jaipur City.
4. To understand Kinetic studies involved in the use of Brick Powder and Marble Slurry Powder.

5. Removal of fluoride by marble slurry powder may cause increase in Ca+ hardness, which will be studied and results will be analysed.

**SCOPE OF THE STUDY**

In the present study, first we'll study physicochemical characteristics including fluoride content of water present in different locations of the Jaipur city. Then an attemt will be made for defluorination of drinking water by employing brick powder and marble slurry powder as new, feasible, effective and low cost adsorbents.

**SIGNIFICANCE OF THE STUDY**

Use of Brick powder and Marble slurry powder as adsorbents in defluorination of water will serve two purposes at the same time, one is low cost and eco-friendly defluorination and other one is waste management. In this study we are trying these adsorbents for different locations of Jaipur City only, but if it works, we can recommend for it anywhere.

**LIMITATIONS**

1. The complete removal of Fluoride content by its adsorption on Brick Powder and marble Slurry powder is not possible.
2. $Ca^{+2}$, $Mg^{+2}$, $Fe^{+2}$, $Ti^{+2}$ ions and particles present in water may interfere in defluorination process, which is not in the scope of the present study.
3. The structural characterization and morphological studies of the adsorbents used demand a separate study to know adsorption mechanism and interdependence of various parameters in a comprehensive manner.
4. In this study we are trying these adsorbents for different locations of Jaipur City only.

**METHODOLOGY**

Brick Powder (BP): Bricks utilized as adsorbent are manufactured in brick kiln situated nearby areas of Jaipur City of Rajasthan state. The brick powder will be washed several times with distilled water till clear water is obtained and dried in oven at $105^{o}C$ for 12 h. The dried material is sieved to obtain particles of size less than 300 μm for the present study.

Marble Slurry Powder (MSP):Rajasthan is the richest state in the country about marble deposits in both quality and quantity. The state is most important centre of marble processing in the country with about 95% of the total processing units. Rajasthan possess large reserve of about 1100 million tones of good quality marble[18].Eighteen districts of the state possess deposits of marble in the form of either extensive or small deposits. The important marble deposits in the state are in Ajmer, Alwar, Banswara, Jaipur, Nagaur, Rajsamand and Udaipur. [19] Solid marble waste, powder and slurry are the major sources of environmental degradation in the areas where marble cutting and processing units are located. The marble waste generation varies widely from 30% by weight (in mechanized mines using wire saw cutting methods for extraction of marble blocks) to 65% by weight (in mines where manual mining is resorted to and the rocks are fractured)[20].Marble Slurry is a suspension of marble fine particles in water, generated during processing, polishing, etc. The average chemical composition of slurry is 28 – 35% CaO, 10 – 14%, MgO, 1 – 2.5% $Fe_2O_3$, 15 -20% acid insoluble and 35 – 40% loss on ignition with traces of titanium oxide and lead. Dry marble slurry powder will be used as a adsorbent.

All studies will be carried out in 250 ml conical flask with 100 ml test solution at room temperature. The absorbant suspensions are equilibriated by shaking in horizontal shaker for different time interval ranging from 15 to 120 minutes and various control parameters like pH, adsorbent dose, initial concentration of fluoride in samples, etc. At the end of the shaking period, the suspension will be centrifuged and filtered using Whatmann filter paper and residual fluoride concentration will be determined in the supernatant liquid by SPANDS method[21] .

Batch study will be conducted to determine the optimum conditions and study the effect of pH, adsorbent dose and contact time on test solutions. The effect of pH on fluoride will be studied by adjusting the pH of test solution using 0.1N HCl or 0.1M NaOH on fixed quantity of adsorbent, while effect of adsorbent dose and contact time are studied by varying dose and contact time respectively. Optimum conditions are selected for further studies. Drinking water samples collected from different locations of Jaipur City of Rajasthan, India will be studied for defluorination under the feasible optimzed conditions to check the suitability of the BP and MSP adsorbent under field conditions.

**Physicochemical Characterization of Drinking Water Samples Before and after Defluorination:**The following parameters will be determined in drinking water samples from various locations of study area before and after Defluorination --- Turbidity, TDS, EC, Total Alkalinity, Total Hardness, Chloride, Fluoride, Phosphate, Sulphate. All values are in ppm (mg/L), except EC in mho/cm, Turbidity in NTU and pH.[12]

**Adsorption kinetics of fluoride removal:**

The rate constant $k_{ad}$ for sorption of fluoride using both of the adsorbent will studied by applying-

$\text{Log } (q_c - q) = \log q_c - k_{ad}\, t/2.303$

Where, $q_c$ and q (both in mg/g) are the amount of fluoride absorbed at equilibrium, at any time (t), respectively

**Effect of pH of samples on removal of fluoride:**

The removal of fluoride using brick powder and marble slurry powder will be studied in the different pH solutions and the results will be compared.

**Effect of adsorbent dose and contact time on removal of fluoride:**

The effect of adsorbent dose and contact time will be studied using brick powder and marble slurry powder and the results will be compared.

**MONTHWISE PLAN OF WORK**

| | |
|---|---|
| August, 2013 to October,2013(03 months) | Review of the Literatures |
| November, 2013 to December, 2013 (02 months) | Collection of water samples |
| January, 2014 to February, 2014 (02 month) | Preparation of adsorbent samples |
| March, 2014 to October, 2014 (8 months) | Experimental performance and data collection |
| November, 2014 to April, 2015 (06 months) | Analysis and interpretation of data and verification of the results |
| May, 2015 to July, 2015 (03 months) | Preparation and submission of report |
| | **Total Time (expected) = 24 Months** |

## MONTH WISE PLAN OF WORK (GRAPHICAL REPRESENTATION)

| **Activity / Months** | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 | 19 | 20 | 21 | 22 | 23 | 24 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Review of Literature | | | | | | | | | | | | | | | | | | | | | | | | |
| Collection of water samples | | | | | | | | | | | | | | | | | | | | | | | | |
| Preparation of Adsorbent Samples | | | | | | | | | | | | | | | | | | | | | | | | |
| Experimental performance and data collection | | | | | | | | | | | | | | | | | | | | | | | | |
| Analysis and interpretation of data | | | | | | | | | | | | | | | | | | | | | | | | |
| Preparation and submission of report | | | | | | | | | | | | | | | | | | | | | | | | |

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